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AN IMPROVED METHOD OF MEASURING MAGNETIC ANISOTROPY OF PARAMAGNETIC CRYSTALS FROM 303°K TO 68°K AND NEW DATA OF SOME Co^{2+} AND Fe^{2+} TUTTON SALTS

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ABSTRACT With a view to increasing considerably the accuracy of the experimental data for the magnetic anisotropies of paramagnetic crystals considerable changes in the design of the existing apparatus, originally constructed by Bose (1947) and later modified by Dutta (1956), was necessary. The main improvements aimed at and achieved in the present set-up are :

1. More than tenfold increase in the sensitivity of the detection (i.e., up to 01°) and measurement of the rotational motion of a freely suspended paramagnetic crystal, by using a photo-electric detecting device and an accurately graduated double-vernier torsion head.

2. A hundred times increase in the stabilization of the magnetic field, i.e., up to 0.01 oersteds.

3. A tenfold increase in the stabilization and accuracy of the temperature of the crystal i.e. up to 0.01 K, by using additional calibration points, a sensitive potentiometric device for measuring the e.m.f. of the thermocouple eliminating spurious e.m.f.'s, and finally using a new type of gas flow cryostat.

The experimental data thus obtained with some ferrous and cobalt Tutton salts, in the temperature range of 303° K to 68° K, show a general deviation from the already existing data of Bose (1947).

INTRODUCTION

In recent years anisotropic ligand field theories of most of the salts of the iron-group elements have been developed by Bose *et al.* (1961, '62, '63, 64), Chakravorty (1964) and others in our laboratory and elsewhere with great rigours. In the case of Fe^{2+} and Co^{2+} Tutton salts, theoretical formulation enables one to express the mean and principal susceptibilities of the paramagnetic complexes in terms of certain parameters connected with the anisotropic ligand field splitting, covalency effect and admixtural effect from the upper orbital levels. In order to evaluate the above mentioned theoretical parameters very accurately and to observe the finer features in their thermal and other behaviors, it was necessary to determine the mean susceptibility and magnetic anisotropy as accurately as possible. Earlier measurements on anisotropies and susceptibilities of some of

these salts are in the nature of pioneering work and the accuracy of the room temperature value as well as at low temperatures are not quite up to the mark of the rigorous theory developed.

With a view to supplying such data, the present anisotropy balance and a new gas flow cryostat have been set up to increase the sensitivity of the measurement, at least ten times the earlier ones, by avoiding carefully the usual sources of errors. In the present paper the crystalline and ionic magnetic anisotropies of the Tutton salts, $Co(NH_4SO_4)_2, 6H_2O$ $Co(KSO_4)_2, 6H_2O$, $Fe(NH_4SO_4)_2, 6H_2O$; and $Fe(KSO_4)_2, 6H_2O$ measured with above set-up are given in the range 68°K to 303°K. These crystals are isomorphous and belong to the monoclinic system with space group P_{2_1}/a, the unit cell containing two magnetically equivalent ions at (0, 0, 0) and $(\frac{1}{2}, \frac{1}{2}, 0)$.

MEASUREMENT OF MAGNETIC ANISOTROPY

The method used for the measurement of magnetic anisotropy is the "Static torque" method of Stout and Gricfel (1950), and Dutta (1956) which is a very useful modification of the "Critical torque" method of Krishnan *et al.* (1935). In this method, the maximum magnetic couple acting on the crystal at 45° position due to the horizontal homogeneous magnetic field H is kept balanced by the torsion of the vertically suspended fibre. The magnetic anisotropy $\Delta\chi$ per gm. mole, in the horizontal plane is related to the maximum torsion angle α_m according to the following expression

$$\Delta\chi = \frac{2MC}{mH^2}\,\alpha_m$$

where M and m are, respectively, the molecular weight and mass of the crystal, and C is the torsion constant of the fibre.

The angle α_m is noted from the vernier torsion disc, from which the crystal is suspended, and the mass m is measured with the help of a Mettler micro-balance (0.5×10^{-6} gms). To determine the constant C/H^2, the value of α_m is measured for a $NiSO_4, 6H_2O$ (tetragonal system) crystal of known mass. The $NiSO_4, 6H_2O$ crystal is suspended with its c-plane vertical and the shape is chosen such that the cross-section in the horizontal plane is approximately a square, to avoid shape effect (M. Mazumdar 1962). The exact value of $\Delta\chi_s$ of this standard crystal at the temperature of the experiment is obtained from an already calibrated graph of $\Delta\chi_s$ vs temperature round about room temperatures, (Dutta 1956) and substitution of $\Delta\chi_s$ in the above equation determines C/H^2.

The anisotropy of a given crystal at any temperature is determined by noting the corresponding α_m at that temperature. In most cases we have observed α_m at intervals of about 20°K between room temperature and 68°K.

In the present work, the crystals to be investigated being monoclinic the crystalline anisotropies are determined by measuring firt the anisotropies with (1) "*b*" axis vertical and then with (2) "*a*" axis vertical or the (001) plane horizontal the planes being well developed in these crystals. The "*b*" axis coincides with the principal susceptibility χ_3 so that the first measurement directly gives the difference $\chi_1-\chi_2$ from the above eqn. The second measurement gives $\chi_1 \sim \chi_3$ using the eqn.

$$\Delta\chi = \pm|(\chi_1 - \chi_3)-(\chi_1-\chi_2)\sin^2\theta|$$

or

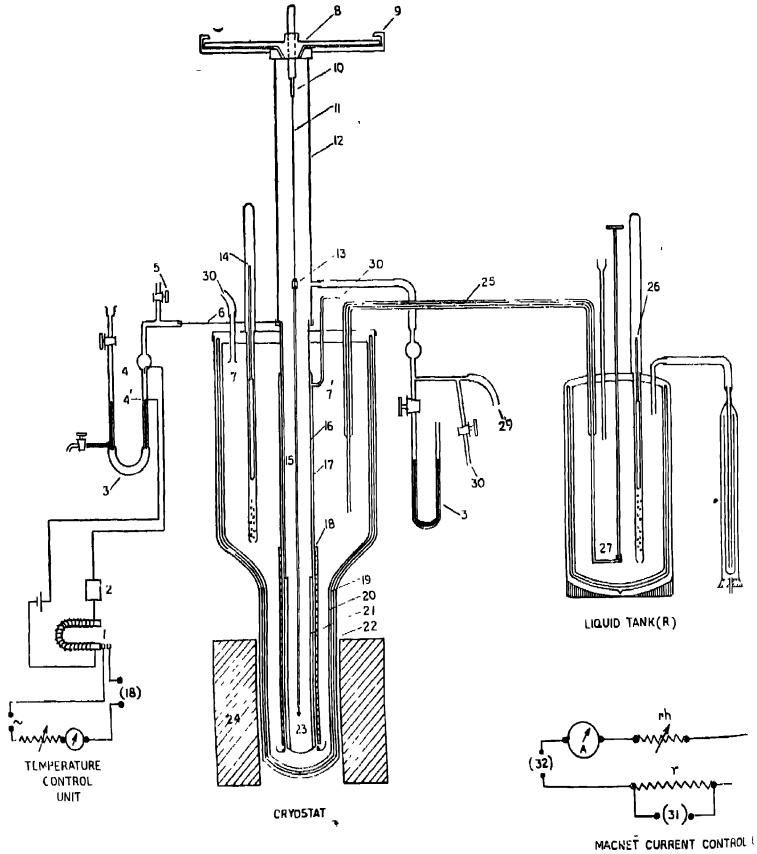
$$\Delta\chi = \pm|(\chi_1-\chi_3)-(\chi_1-\chi_2)\cos^2\theta|$$

according as the "*a*" axis is vertical or the (001) plane horizontal is considered. The +ve or − ve sign is taken as "*b*" axis sets perpendicularly or parallel to the magnetic field in these latter suspensions. The angle θ between χ_2 and "*a*" axis is determined as described by previous workers Dutta (1954), in this laboratory.

THE IMPROVEMENTS IN THE PRESENT SET-UP FOR MAGNETIC ANISOTROPY MEASUREMENT AS COMPARED TO THE PREVIOUS WORKS

The magnetic anisotropy of any paramagnetic crystal is determined by comparison with the magnetic anisotropy of $NiSO_4$, $6H_2O$ taken as standard, and as such it is essential that the magnetic field should remain constant during the comparison. Furthermore since the magnetic couple on the crystal due to the magnetic field depends upon the square of the magnetic field, even a small fluctuation in the field during measurement of the rotation of the crystal affects the observed values of anisotropies appreciably. In earlier experiments here the magnetic field was kept constant only within 0.1%. For keeping the field constant to a much better degree, a potentiometric device is used to stabilize the d.c. feeding the magnet. The magnet current is obtained from a compound wound 220 d.c. generator, the 15 K.W. 440 A.C. motor of which is stabilized with a suitable saturated core transformer so that the voltage of the generator is constant within 1/4 volt. For the final stabilization of the magnet current a small standard resistance '*r*' is added in series with the coils of the electromagnet. The p.d. across this standard resistance '*r*' is maintained constant within 1 micro-volt by the usual potentiometric balancing method, controlling the current through '*r*' by adjusting a fine control wire rheostat '*rh*' in series with it (see Fig.).

The maximum current that can flow through the coils in series with the magnet is 1.6 amps. and hence the value of the standard resistance was chosen so as to create a p.d. of exactly 1.01830 volts across it when a current of about 1.56 amps (it is not necessary to measure this current exactly) flows through it. The standard resistance (~0.65 ohms) was prepared by winding a Eureka wire (1.5mm dia.) over an ebonite core and the ends soldered to the leads.



(1) relay magnet (2) transistorised amplifier (3) mercury manometer (4 4') platinum electrod (5) stop cock (6) stainless-steel capillary tube (7,7') outlets for oxygen (8) torsion-head (9) vern (10) pin-holder (11) quartz-fibre (12) experimental chamber (glass portion) (13) mirror-syst (14) indicator (15) suspension system (16) experimental chamber (metallic portion) (17) co-axial hi (18) heater coil (19) glass-dewar (20) inner-casing (21) constant volume gas thermometer (22) ou casing (23) crystal (24) pole-pieces (25) siphon (26) indicator (27) pin-valve (28) di (29) to Kipp's apparatus (30) to pump (31) to potentiometric circuit (32) to magnet coils.

The low frequency fluctuation of the magnet current are automatically damped by the magnet inductance and any residual effect of the same upon the crystal is damped by the low (non-resonant) natural time period of the suspension system. Hence the magnetic couple balance reading and the magnet current balance reading can be synchronized to within a fraction of a second depending upon the personal reflex action of the observer so that if the observer is all the while assured that neither the potentiometric current balance nor the magnetic couple balance has fluctuated from the desired value appreciably over several seconds during the final adjustments of the controls it is easy to see that the steadiness of the magnet current is limited only by the error of the least reading of the balancing circuit microammeter (of small resistance) Estimating this it is found that the stabilization of the magnet current during measurement is attained to within 1 part in 100,000. Of course, it should be remembered that owing to leakage currents the absolute value of the magnetic field may not be obtained with the same degree of accuracy, but since our anisotropy measurements is a relative one this will not matter unless the leakage current has different values during a set of measurements, which is rather unlikely.

PREPARATION AND MOUNTING OF CRYSTALS

Single crystals of ferrous and cobalt Tutton salts $[M^2(M^1SO_4)_2.6H_2O]$ were prepared by slow evaporation from a saturated solution containing equimolecular weights of analytically pure component salts of Merck or BDH quality in double-distilled water The solution was allowed to evaporate in a dust-free air-conditioned room on a vibration-proof stand Out of successive crops of crystals from the same mother liquor only the middle ones were chosen. Single crystals thus obtained were allowed to crystallise for the second or even the third time if thought necessary Such repeated crystallisation reduced the impurities in the crystal to a minimum The crystals selected were next tested under a polarising microscope so as to reject any twinned or defective crystals. One of the best crystals thus obtained was next attached to the end of a thin and light glass-rod with 'Quick-fix' adhesive (diamagnetic and non-crystalline), in the required orientation with reference to the rod, correctly to 0.1 degree by mounting the whole on a two-circle goniometer. The rod bearing the crystal was next attached to the lower end of a thin and long glass tube, fitted at the top with a small light hexagonal mirror system (13) (fig.) with the hexagonal axis vertical. This whole suspension system (15) was next attached to quartz-fibre (11), of suitable diameter depending on the magnetic anisotropy of the crystal, from the pin (10) fixed axially to the torsion head (8) The torsion head is a brass disc of 16cms diameter, fitted on a smooth taper collar, and very accurately graduated into 500 equal divisions, the two verniers (9) (with vernier constant 0 02 of each main scale division, i.e. ~0 014 degrees, in earlier experiments this was 0.1 degree) are carried on a pair of radially projecting arms connected to the collar, diametrically opposite each

other on the outer edge of the disc. A pyrex glass tube (diameter 3cms, length 24 cms) is fitted into a circular groove on the lower end of the collar, and cemented air tight by araldite adhesive. The other end of this glass tube is fitted air tight to the german silver end of the experimental tube (16), inside the cryostat by a metal glass joint. Thus the experimental chamber is composed of a glass portion (12) above, through which the hexagonal mirror attached to the crystal suspension is visible, and a metallic portion inside the cryostat. The crystal to be measured, hangs near the lower end of metallic portion

To prevent condensation of the atmospheric moisture, or carbon dioxide upon the sample crystal at low temperatures (down to about 65°K), the experimental tube was evacuated and filled with hydrogen gas at atmospheric pressure through a side tube from a Kipp's apparatus, after passing through a series of purifying and drying towers. The pressure inside the experimental chamber was kept constant at low temperatures

DETECTION OF CRYSTAL MOTION BY PHOTO-CELL ARRANGEMENT

It has been seen in earlier experiments that the rotational motion of the crystal in the magnetic field is considerably magnified by the motion of a collimated beam of light from a stabilized a c source, reflected from one or the other mirrors of the hexagonally arranged mirror system attached to the suspension rod. But, since the maximum angular motion of the crystal is through 45° from the no-torque position to the maximum torque position in the magnetic field, it is essential that both these angular positions should be adjusted and measured so accurately so as to keep the error in $\sin 2\phi$ (Dutta, 1956) to less than one part in 10,000 For this purpose now, a pair of barrier-photo-voltaic cells, connected in opposition through a suitably shunted sensitive galvanometer, are mounted very close to each other and kept inside a long blackened wooden box with a small window in front, through which the light spot falls on the cells

The position of the photo cells, placed at a distance of about 50 cms from the mirror system, is adjusted in such a way that the cells are very nearly equally illuminated, so that no resultant e.m.f. is observed in the galvanometer Now, if the mirror rotates even by a small amount by applying the magnetic field on the crystal, the balance of the photo-cell e.m f is destroyed and a large deflection is observed in the galvanometer. The balance is restored by applying a sufficient torque upon the quartz fibre bearing the crystal, with the help of the torsion head.

The magnification was adjusted in such a way that even if the crystal rotates through 0.01°, (which is roughly equal to the value of one vernier division of the torsion head), the galvanometer deflection on the scale is about 10 cms. The current into the galvanometer is controlled by a 5 K Ω potentiometer. It will be seen that, even with a heavily shunted galvanometer, the sensitivity of the detection of the rotation of the crystal is more than 20 times the earlier lamp and scale

method and more than 100 times as can be measured with the present torsion head. There is thus scope for further increase in accuracy of measurement, if needed in future works.

CRYOSTATIC ARRANGEMENT

The cryostat is really a combination of gas flow type (Bose 1947) and liquid bath type (Bose *et al.* 1963) At temperatures between 303°K and 90°K, it acts as a continuous gas flow type, the flow of cold gas from evaporated liquid oxygen being controlled by an adjustable speed pumping arrangement After reaching the liquid oxygen temperature i.e. 90°K, a quantity of liquid oxygen is collected inside the cryostat and made to boil inside it under reduced pressure, whereby ~68°K is obtained in the experimental chamber.

The present cryostatic arrangement differs considerably in details of construction from the earlier types. The cryostatic arrangement broadly consists of three main sections, (Figure)

i) The liquid oxygen reservoir tank R, with vacuum jacket cover.

ii) The cryostatic chamber, connected to the pumping unit

iii) The temperature controlling unit

i) *Liquid oxygen reservoir tank R*

The tank *R* is a cylindrical chamber of german silver of capacity 2 litres and fitted with a cap packed with a lining of cotton and felt, and placed inside a wide-mouthed hard glass thermo-flask. The cap has two openings, through one of which liquid oxygen is poured, and through the other dry air is allowed into the tank, to replace the liquid air sucked out. A light glass bulb (26) ending in a long thin capillary stem with an index at the top passes through a perforated german silver tube extending nearly to the bottom It floats in liquid oxygen, the end of the stem being visible through a gauge glass tube, fitted to the upper end of german silver tube It serves as the liquid level indicator.

Liquid oxygen is sucked into the cryostat chamber with the help of a two-stage rotary oil pump of 50 litres/min. gas capacity through a vacuum jacketted german silver siphon, the flow being controlled by a needle valve (27) The siphon is a double-walled tube of german silver, the interspace being evacuated and sealed permanently and is bent twice at right angles as shown in the figure To obtain temperatures below liquid oxygen b.pt the needle valve is operated with a long thin stainless steel tube stem and can be used to regulate the flow of liquid into the cryostat, as also to cut off completely the supply after a sufficient quantity of liquid has been sucked into the cryostat, when it can be made to boil under reduced pressure inside the cryostat

ii) *Cryostat*

The cryostat is a wide mouthed (inner dia.~10 cms.) double-walled silvered glass Dewar (19) with a narrow tail (inner dia ~3.5 cms.) which passes into the

space between the polepieces (24) of the magnet. An outer brass casing (22) protects the glass dewar from external mechanical shocks another inner german silver casing (20) serves to protect it from breakage due to sudden local cooling when oxygen is pumped into it. Both are fitted with leak-tight caps, the space between the caps being lined with aluminium foil and packed with felt to prevent heat leakage. One bent of the siphon (25) passes through the caps into the inner chamber, the other bent end passing into the reservoir R, its inner tube passing to the bottom. A glass float-indicator (14) as used in the tank R is also fitted to the cryostat chamber to see the level of the liquid oxygen when the cryostat is used as a bath type one as earlier mentioned.

The experimental chamber (16) as mentioned earlier reaches up to 2 mms from the bottom of the narrow tail end of the cryostat. The portion of (16) above the tail of the dewar is made of german silver to prevent conduction of heat through the neck into the dewar. The remaining portion lying inside the tail of the dewar is made of copper to help temperature uniformity, the two parts being silver soldered. The copper tube has an annular chamber near the lower end which acts as the bulb for a constant volume gas-thermometer (21). A stainless steel capillary tube (6) from this bulb passes out of the experimental chamber and is connected to a mercury-in-glass manometer (3), the junction of the two being made leak-tight with araldite. The composite experimental tube (16) is surrounded by a coaxial copper jacket (17) open at the lower end and soldered to (16) at the top, an inch below the inner cap, and a side tube (7′) of stainless steel, leads from this jacket to the pump. A fine nichrome coil (18) insulated with thin mica sheet is wound non-inductively for about 10 cms of the lower end of this tube (17), and fed by a small a.c. from the mains through a variac. This acts as a heater, the insulated leads of which are brought out through the caps and sealed leak-tight with araldite cement (not shown in the fig.). Thin copper gauze of about 20 mesh per inch, is loosely packed over the heater and also in the wider portion of the dewar to facilitate rapid and uniform evaporation of liquid oxygen and quick and uniform distribution of heat over the experimental chamber. The cold vapour from liquid oxygen after exchanging heat with the heater and arriving at a desired low temperature is sucked into the narrow space between the experimental chamber and the coaxial jacket, cooling the former and finally goes out of the cryostat through the suction line (7′). The heat-exchange between the experimental chamber and the vapour depends on the rate of pumping so that different steady temperatures are obtained in (16) with a fair degree of accuracy, by regulating this rate. The temperature regulation is further helped by adjusting the heater current. Since the rate of pumping cannot be adjusted beyond a certain limit owing to the irregular spurts of liquid oxygen through the siphon, caused by the somewhat intermittent suction of the rotary pump and also by the back pressure developed in the siphon line by the evaporation of the liquid a relay

system worked by a gas thermometer is utilized for fine control of temperature, as will be described later

For obtaining temperatures below 90°K. outlet (7′) is nearly closed and the alternative outlet (7) is fully opened. The outlet (7) is connected to the pump in parallel to (7′), and reaches only an inch below the cap of the inner casing of the dewar. Liquid oxygen is now pumped into the cryostat by opening the pin valve (27) full, and then closing it tightly after a sufficient amount of the liquid is collected as shown by the level indicator Liquid begins to boil under the reduced pressure which can be noted by a manometer (not shown in the fig) connected to the cryostat chamber A steady temperature is soon reached depending on the steady pressure over the liquid The heat leakage in our system being fairly large it was not possible with the given pump to go below about 68° K by reducing the vapour pressure.

(iii) *Temperature control*

The temperature inside the experimental tube (16) is very accurately controlled by means of a gas thermometer (H_2 gas from a Kipps can be used over the entire range) relay system The bulb of the constant-volume-gas thermometer connected to the manometer as mentioned earlier (fig) can be opened to the source of gas through the stop-cock (5) Two platinum electrodes (4) and (4′) are fused into the capillary glass tube forming one limb of the manometer (3), (4′) always dips into the mercury. When the mercury level touches the other contact (4) the relay magnet circuit is completed, which in its turn closes the heater circuit.

Initially by adjusting the pumping rate, while keeping the stop-cock (5) open to the atmosphere, the temperature required is nearly attained with a slight preponderance of cooling, and then the stop-cock is closed, shutting off the bulb from the atmosphere The enclosed gas in the bulb now contracts due to the small tendency for over cooling, the mercury level rises and makes the contact when the heater is adjusted as far as possible to just balance the overcooling so that a fine control of temperature, to less than 0.01° K is obtained.

This adjustment is however laborious and is likely to be upset by fluctuations in the pumping rate or the heater current, and hence need not be made very critical What is done in practice is that with a slight cooling tendency the heater current is adjusted to just overbalance it, so that the relay, actuated by the gas thermometer makes and breaks the heater circuit repeatedly, to just maintain the balance of temperature. With suitable adjustments the alternate peak of rise and fall in temperature can be narrowed down to less than 0.01°K as indicated by the fluctuation in the light spot in the galvanometer (not shown in fig.) used to indicate the balance of the copper-constantan thermo-couple e.m.f. in the potentiometric circuit for the temperature measurement.

TEMPERATURE MEASUREMENT

The temperature of the crystal is measured by means of a very accurately calibrated copper-constantan thermo-couple junction placed very near it, the temperature gradient in this region being found to be less than 0·01°K. The thermo-couple leads come out of the experimental chamber through a leak tight side tube (not shown in the fig.)

The thermo-couple was calibrated using a 5 constant formula relating the thermo-e.m.f. E' to the centigrade temperature 't' of the measuring junction, (the standard junction being kept in melting ice), as follows :—

$$E' = a + bt + ct^2 + dt^3 + et^4$$

where a, b, c, d, e, are constants determined by noting the thermo e.m.f. at the standard temperatures of ice steam, solid CO_2, room temperature (given by a standard mercury glass thermometer), and liquid oxygen boiling point at atmospheric pressure. *When both junctions are put in melting ice mixed with distilled* water in a thermo-flask, then

$$E = a = 0$$

showing there were no spurious e.m.f.'s. For obtaining the temperature of pure liquid oxygen, a miniature rectifier column was constructed and used for purifying the commercially obtained liquid oxygen containing some dissolved nitrogen. Oxygen gas from a cylinder of 99·5% purity at ~100 atoms. pressure, was precooled by circulating through a cooling spiral immersed in a reservoir of commercial liquid oxygen at the bottom of the rectifier column and after liquefaction by Joule-Thomson expansion at the top of the column, is made to trickle down a series of perforated discs made out of fine mesh of copper gauze, thereby exchanging its nitrogen content with the oxygen content of the upstreaming vapour mixture of oxygen and nitrogen from the reservoir. Thus the escaping gas becomes progressively richer in nitrogen, while the down flowing liquid richer in oxygen, until the liquid in the reservoir is practically all pure oxygen. The thermo-couple immersed in this liquid shows a gradual reduction in e.m.f. until at the end it becomes steady at pure oxygen temperature. The corresponding pressure inside the rectifier over the liquid is noted, as also the barometric pressure on a standard Fortin's barometer, for correcting to the normal boiling point.

Solid CO_2 temperature is obtained with a mixture of ether and solid CO_2 made by expansion from a commercial cylinder of the gas of sufficient purity. Steam temperature is obtained in the usual manner in a hypsometer. Both temperatures are corrected for the atmospheric pressure in the usual way.

To calibrate the thermo-couple from 90°K to 68° K, we have measured thermo-e.m.f. at different vapour pressure of liquid nitrogen. The corresponding temperatures are obtained from the International Critical Table (Vol. III). The

vapour pressure of the boiling liquid was measured by means of a Torricelli type of Hg manometer, capable of reading up to 0·5 mm of the mercury level. Near the temperature 68°K, 1 mm change of the level corresponds to 0·03°K, so that the accuracy of the temperature is 0·015°K. For temperatures above, the accuracy increases as can be shown from the vapour pressure chart.

TABLE I

Sound no of crystals	Mass of crystal m (gm)	Maximum torsional angle α_m (degree)	α_m/m at 301·23°K
1	0·043495	67·22	1545·46
2	0·022043	34·02	1543·42
3	0·043200	67·70	1547.23
4	0·025009	37·34	1546·64
5	0·039194	60·52	1544.11

TABLE II

$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$

Temp (°K)	Angle θ° between 'a' & χ_2 axes	$(\chi_1-\chi_2)$ $\times 10^6$	$(\chi_1-\chi_3)$ $\times 10^6$	$(K_\parallel-K_\perp)$ $\times 10^6$	(ΔKT) $\times 10^4$	ϕ° Angle
303	−36 92	2381 6	180 45	4582.7	1388 8	43 86
280	−36 74	2826 5	234 69	5418 3	1517 1	43 75
260	−36 54	3278 1	288 46	6207 7	1629 6	43 68
240	−36 35	4038 2	351.56	7724 8	1853 9	43 70
220	−36 22	4942 2	419 42	9464 9	2082 3	43 75
200	−36 18	6040.0	502 50	11577	2315.5	43 75
180	−36 15	7413 6	604 94	14222	2560 0	43 78
160	−36 11	9246.1	737.50	17755	2840.7	43 80
140	−36 10	11750	908 16	22592	3162.8	43.85
120	−36 09	15377	1151 4	29404	3528 5	43 85
100	−36 08	20520	1518 0	39522	3952 2	43 90
80	−36 08	29062	2125 0	56000	4480.0	43 91
68	−36 08	37737	2724.9	73751	5015 0	43 93

TABLE III

$FeSO_4$, K_2SO_4, $6H_2O$

Temp. (°K)	Angle 0° between 'a' & χ_2 axes	$(\chi_1-\chi_2)$ $\times10^6$	$(\chi_1-\chi_3)$ $\times10^6$	$(K_\parallel-K_\perp)$ $\times10^6$	(ΔKT) $\times10^4$	$\phi°$ Angle
303	−43.90	1768 2	− 301 18	3837.6	1162 8	42 75
280	− 44 00	2028 1	−391 32	4447 5	1245 3	42.46
260	−44 11	2304 7	−485 65	5095.1	1324.7	42.23
240	− 44.25	2644 9	−601 73	5891.5	1413.9	42.06
220	−44 45	3065.1	−753 51	6883 7	1514.4	41.85
200	−44.75	3597.5	−948 50	8143.5	1628 7	41.65
180	−45 02	4274 7	− 1214.5	9763.9	1757.3	41.41
160	−45.44	5171.9	−1544.9	11889	1902.2	41.26
140	−45.85	6397.9	−1922.4	14718	2060.5	41.25
120	−46.18	8125.0	−2438.2	18688	2242.5	41 25
100	−46.25	10707	−3054.0	24469	2446.9	41.41
80	−46.30	14847	−3570.0	33265	2661.2	41 91
68	−46.30	18386	−4300.1	41071	2792.3	42 00

TABLE IV

$CoSO_4$, $(NH_4)_2SO_4$, $6H_2O$

Temp. (°K)	Angle 0° between 'a' & χ_2 axes	$(\chi_1-\chi_2)$ $\times10^6$	$(\chi_1-\chi_3)$ $\times10^6$	$(K_\parallel-K_\perp)$ $\times10^6$	(ΔKT) $\times10^4$	$\phi°$ Angle
303	60.10	3011.8	1715 4	4308 2	1305.3	33.26
280	60.04	3565.7	2108.4	5023.0	1406.4	32.58
260	60.03	4156.8	2510.3	5803.3	1508.8	32.18
240	59.98	4878.5	3001.7	6755.3	1621.2	31.80
220	59.90	5760.3	3617 7	7902.9	1738.6	31.36
200	59 80	6872.5	4400 0	9345.0	1869 0	30.95
180	59.65	8283.9	5401.2	11166.	2009.8	30.53
160	59 38	10105	6742.2	13468	2154.8	29.98
140	59 07	12515	8576.5	16453	2903.4	29.28
120	58 07	15652	10930	20374	2444.8	28.75
100	58.35	19550	14502	24598	2459.8	26.93
80	58.27	24500	18300	30700	2456.0	26.23
68	58.25	27898	21622	34174	2323.8	25.33

TABLE V

$CoSO_4$, K_2SO_4 $6H_2O$

Temp (°K)	Angle θ° between 'a' & χ_2 axes	$(\chi_1-\chi_2)$ $\times 10^6$	$(\chi_1-\chi_3)$ $\times 10^6$	$(K_{\parallel}-K_{\perp})$ $\times 10^6$	(ΔKT) $\times 10^4$	$\phi°$ Angle
303	30 20	2490 5	1835.2	3145.8	953 17	27 15
280	29.90	2913.9	2152 0	3677 8	1029 7	27 08
260	29 65	3357 9	2502 3	4213.5	1095.5	26.78
240	29 45	3890 6	2940 2	4861 2	1166 6	26 30
220	29 25	4532.2	3530 0	5552 1	1221 4	25 16
200	29 06	5317 5	4306 4	6328 6	1205.7	23.55
180	29 00	6311.7	5185.1	7438 3	1338 9	22.90
160	29.00	7562.9	6190 2	8934 8	1429 5	23 06
140	29.00	9198.9	7538 8	11059	1548 2	23 51
120	29 00	11451	9218.9	13653	1638 3	23 68
100	29.00	14320	11501	17139	1713 9	23.91
80	29 00	18328	14403	22253	1780.2	24 83
68	29 00	21907	16552	27262	1853 8	26.30

SENSITIVITY OF THE APPARATUS

To check the reproducibility and accuracy of our measurement, we have measured the magnetic anisotropy of 5 crystals of $NiSO_4$, $6H_2O$. The ratio of α_m/m of these crystals were found to be constant to about 2 parts in a thousand, (Table I) This variation is more due to lack of perfection in the different crystals rather than due to inaccuracy in other experimental parameters, since it was found that for the same crystal the said ratio is constant up to 2 parts in 10 000 when the same crystal is measured by varying other conditions such as detaching and remounting it, changing the torsion fibre and also the magnetic field, taking into consideration the changes in C and H

TABLES OF RESULT

The method of calculation of the principal crystalline anisotropies at different temperatures is already described earlier. The first 4 columns of the Table II to V respectively, give (i) the temperatures in degrees Kelvin, of the experimental measurements, (ii) the angles between "a" axis and χ_2 direction of the crystals, (iii) the values of $\chi_1-\chi_2$ and (iv) values of $\chi_1\sim\chi_3$ calculated from the extrapolated graphs at 20°K intervals, starting with 303°K and ending at 68°K, the lowest available temperatures.

It has been shown from earlier works, (Bose *et al.* 1960, Bleaney and Ingram 1951) that the complexes $Fe^{2+}\cdot 6H_2O$ and $Co^{2+}\,6H_2O$ in the Tutton salts have nearly tetragonal symmetry and moreover, the symmetry axes of the two octahedra in the unit cell are inclined at an angle which is bisected by χ_1 axis of

the crystal. Hence the principal gm. ionic anisotropy of the complexes is given by

$$K_{\parallel} - K_{\perp} = 2(\chi_1 - \chi_2) - (\chi_1 - \chi_3) \quad \text{for } K_{\parallel} > K_{\perp},$$

and

$$\cos 2\phi = \frac{\chi_1 - \chi_3}{2(\chi_1 - \chi_2) - (\chi_1 - \chi_3)}$$

where $K_{\parallel}$ and $K_{\perp}$ are the principal gm. ionic susceptibilities parallel and perpendicular to the tetragonal axis of the complex. The values of $(K_{\parallel} - K_{\perp})$ and ϕ calculated in this way at different temperatures are given in the next two columns of the tables. The overall accuracy of these values is estimatedd as better than 0.1%. This is at present limited by the method of graphical extrapolation adopted but can be very much improved by using a more laborious least square method. But since our approximation in respect of the symmetry of the complexes has already been assumed it was not thought worth while for the present to perform this extra labour in the absence of more accurate structural data.

RESULTS AND DISCUSSION

(a) *The shape of the magnetic ellipsoid of the crystals*

From the values of $(\chi_1 - \chi_2)$ and $(\chi_1 - \chi_3)$ it will be observed that in the Fe^{2+} salts the magnetic ellipsoid of the crystals are roughly reduced to oblate spheroids about the χ_2 axis, which has thus the minimum susceptibility. This is evidently a consequence of the fact that $K_{\parallel} \gg K_{\perp}$ and the angle ϕ is close upon 45°. The former conclusion that $K_{\parallel} > K_{\perp}$ in the case of potassium salt is directly a consequence of our observation that $\chi_1 - \chi_3$ is negative for this salt at all temperatures. In consequence, in this case the condition that ϕ is nearly 45° is also automatically fulfilled as is shown from our calculations of ϕ. The alternative assumption of $K_{\perp} > K_{\parallel}$ leads to a value of $\cos 2\phi > 1$, which is impossible. For the ammonium salt, however, the conclusion is not so straightforward, and we assume the same to be true also in this salt, not only because this is more likely for an isomorphous salt with the same paramagnetic ion, but because, as shown by Bose *et al.* (1961) such an assumption (i.e. $K_{\parallel} > K_{\perp}$) will lead to a particular energy level scheme in this salt leading to the anisotropic spectroscopic splitting factors to be $g_{\parallel} \simeq 9$, $g_{\perp} = 0$. (Bose *et al.*, 1960) which agrees with the experimental result.

For the Co^{2+} salts the crystalline tensor ellipsoid is more or less triaxial as can be seen from the anisotropic data and hence the ambiguity is more difficult to remove normally. But in this case for both the Tutton salts paramagnetic resonance gives clear indication that the ionic ellipsoid is nearly uniaxial, also, $K_{\parallel} > K_{\perp}$ and the values of ϕ obtained from resonance, (Bleaney, 1951) are close to ours, calculated from magnetic anisotropy. It is, however necessary that we should make more extensive trial and error calculations for finding the actual scheme of energy levels in the individual Tutton salts with the present new and

very accurate data for then we can make a definite decision in favour of one or the other

The detailed discussion of the results in reference to the theory of octahedral Co^{2+} and Fe^{2+} ions will be given in the next part of the paper only after the mean susceptibilities are measured with comparative degree of accuracy which are in progress. It will be, however interesting to give here some broad features of the thermal magnetic behavior of the crystals

(b) *Large ionic anisotropies*

Due to the predominent cubic component of the electric field of the 6 surrounding charges the free-ion ground state $^5D(3d^6)$ of Fe^{2+} breaks up into an orbital triplet and a doublet and the free-ion ground state $^4F(3d^7)$ of Co^{2+} splits into 2-orbital triplets and a singlet a triplet lying lowest in both cases The axial component of the ligand field and spin-orbit interaction considered together, breaks up partially the remaining spin and orbital degeneracies Thus spin-orbit interaction has got a definite effect on the cubic ground level In the first order, unlike some other octahedrally coordinated salts of the iron group such as of Cu^{2+} Ni^{2+} Cr^{2+} and Mn^{2+} This explains the large value of the ionic anisotropy of the octahedrally coordinated Fe^{2+} and Co^{2+} ions in comparison to that of the latter ions the values at 303°K being respectively 4583, 3838, 1308, and 1146 units for $Fe(NH_4SO_4)_2 \cdot 6H_2O$ $Fe(KSO_4)_2 \cdot 6H_2O$ $Co(NH_4SO_4)_2 \cdot 6H_2O$ and $Co(KSO_4)_2 \cdot 6H_2O$. These results agree in general with those of earlier works (Bose 1947 Dutta 1956) but are more accurate as to the actual values as already stated

(c) *Temperature variation of anisotropies*

From the results it is apparent that the ionic anisotropy does not follow a simple linear inverse temparature dependence In many salts of the iron group, previous workers (Bose *et al* 1948 Dutta, 1956), have represented the ionic anisotropy by a 3-constant formula as follows

$$K_{\parallel} \sim K_{\perp} \quad A + B/T + C/T^2.$$

Although we cannot assume that the 3-constant formula is sufficient to fit our experimental results, we expect that the same formula will also hold good in our case. The constant A, B, C are very much structure sensitive and varies from salt to salt even for the same ion It is known that the effect of the distant atoms outside the primary ligand cluster, the disposition of which is determined by packing of the atoms consistent with the space group symmetry of the crystal, is more pronounced in the anisotropy value than in the mean susceptibility (Van Vleck 1939 Bose *et al*., 1957 1958) The members of $Co^{2+}.6H_2O$ or $Fe^{2+}.6H_2O$ clusters are rigidly bound together as shown by the persistence of the cluster under extreme conditions, but not so for the distant atoms which are weakly bound. Consequently even a small anisotropic thermal expansion of the lattice, affects more the effect of the distant atoms i.e., the anisotropic component rather

than the cubic component of the field. The increase of the anisotropy between 303°K and 68°K is observed to be maximum in $Fe(NH_4SO_4)_2\,6H_2O$, being 16 times, and a minimum in $Co(NH_4SO_4)_26H_2O$, being 7 times.

(d) *Variation from salt to salt*

The above effect of the distant atoms also explains the variation of anisotropy values for the same ionic cluster but with a different alkali radical outside it. The difference in the anisotropy value between the two ferrous ions is 20% and between that of cobalt is 36 %

(e) *Change of orientation of the magnetic ellipsoid with temperature*

The change in the angle θ between the χ_2 axis and the 'a'' axis over the entire temperature range is different for each of these Tutton salts, a minimum for $Fe(NH_4SO_4)_26H_2O$ ($\Delta\theta$ - 0.87°) and maximum for $Fe(KSO_4)_26H_2O$($\Delta\theta$ = 2.4°), for the Co^{2+} salts, $\Delta\theta$ = 1.85° and 1.20 respectively for ammonium and potassium radicals. This indicates a small rotation with temperature, of the crystalline magnetic ellipsoid about the crystalline symmetry axis

From the table it is observed that the angle 2ϕ between the 2 tetragonal axes of the differently oriented ions in the unit cell changes with temperature, differently for different salts. For ferrous ammonium, ferrous potassium and cobalt potassium salts, ϕ decreases to a minimum at temperatures 260°K, 140°K and 180°K respectively. However, for cobalt ammonium salt ϕ continuously decreases with temperature The maximum changes $\Delta\phi$ for the above salts taken in the same order, are respectively 0 16', 1 50', 7.90° and 4 25°. The appreciable changes in ϕ for the cobalt ions may be due to the lack of a perfect uniaxial symmetry which we have assumed for calculating ϕ. The changes in θ and ϕ angles are due to anisotropic thermal expansion of the lattice, the ϕ angle being more sensitive to temperature variation

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